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Theoretical and Computational Studies of Rare Earth Substitutes: A Test-bed for Accelerated Materials Development

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Theoretical and computational studies of rare earth substitutes: a test-bed for accelerated materials development

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Abstract

Hard permanent magnets in wide use typically involve expensive Rare Earth elements. In this effort, we investigated candidate permanent magnet materials which contain no Rare Earths, while simultaneously exploring improvements in theoretical methodology which enable the better prediction of magnetic properties relevant for the future design and optimization of permanent magnets. This included a detailed study of magnetocrystalline anisotropy energies, and the use of advanced simulation tools to better describe magnetic properties at elevated temperatures.

Background and Research Objectives

Hard permanent magnets, or ferromagnets which can perform useful work on their surroundings due to their propensity to resist the destruction or reorientation of their magnetic moments, are used widely in industrial applications (e.g., electromagnetic motors in hybrid vehicles, wind turbines). These materials are often variants of Sm_2Co_{17} or $Nd_2Fe_{14}B$, both of which contain Rare Earth (RE) elements. Following former Energy Secretary Chu's Critical Materials Strategy [Chu, S. (2011)], it has been recognized that less-expensive RE-reduced or RE-free alternatives must be found to ensure our worldwide economic competitiveness. In the search for new hard permanent magnets, several figures-of-merit are known to be important, one of which is the magnetocrystalline anisotropy energy (MAE), the energy to rotate the electron spins from easy to hard-axis directions. A large MAE is desired if the material is to possess magnetic domains which themselves resist reorientation when bathed in an external magnetic field emanating from a nearby magnet. Another property is the Curie temperature (T_C), or indeed any magnetic property at temperatures approaching T_C, since the operating temperatures of electromagnetic motors are typically well above room-T. While theoretical and simulation techniques exist to predict these properties, true predictive capability is

sorely lacking, due to the subtle dependence of these properties on the electronic structures of the complex materials involved. It was therefore our aim to survey these areas, while developing new prescriptions for the rapid and accurate computation of permanent magnet properties which may better enable the prediction of trends when composition and temperature are varied.

In the course of this project, we conducted detailed ab initio theoretical investigations of the composition-dependence of MAE for the RE-free alloy, $(Fe_{1-x}Co_x)_2B$ [Daene (2015)], explored the electronic structure and magnetic properties of so-called high-entropy alloys containing up to five elements [Troparevsky (2015)], studied various means of decomposing the MAE into few-site contributions [Aberg (2015)], and developed a new scheme to compute the temperature-dependence of magnetic properties (such as MAE) in compounds with induced local moments. We also studied two features of the interaction between magnetism and atomic structure: The temperature-dependence of phase transition kinetic barriers in uniaxially-compressed iron [Surh (2015)], and the relationship between the MAE and a magneto-elastic high-spin to low-spin (HS-LS) transition in YCo_5 [Benedict (2015)]. While the results of some of these studies were inconclusive, this broad set of investigations allowed us to develop the necessary tools and understanding needed to aid LLNL's ongoing efforts in the area of Critical Materials research.

Scientific Approach and Accomplishments

MAE of $(Fe_{1-x}Co_x)_2B$: The MAE of a material is chiefly due to the interplay between the spin-orbit (SO) interaction, a consequence of fact that electrons in high angular momentum states orbit at relativistic speeds, and the crystal-field effect which arises from the directional bonding in crystals. The smallness of the SO interaction, relative to typical chemical bond energies, renders the MAE difficult to calculate accurately. Moreover, materials with large magnetic moments and sizable MAEs are often those possessing narrow-band electronic states which are notoriously difficult to treat within mean-field electronic structure theories. The alloy $(Fe_{1-x}Co_x)_2B$ is a welcome counterexample in at least certain respects; no narrow f-band elements are present, and it is also the case that the MAE of this system is

known experimentally throughout the entire range of Co-compositions (x), thereby providing a test-bed for ab initio theory. Using DFT, we computed MAE(x) using periodically repeated supercells, and found trends that are similar to the experimental results. Namely, the c-axis of this tetragonal material is the easy axis (favoring permanent magnet applications) for the (70%) Fe-rich material, while the Co-rich side favors planar anisotropy. A major focus of our work was to investigate the effects on the MAE of both local lattice relaxations (shown to be small) and preferential ordering (shown to be more important on the Co-rich side). We also compared our results to those of other theoretical treatments of alloy disorder such as the Coherent Potential Approximation (CPA), in which multiple-scattering theory is used to model statistically uncorrelated Co-Fe disorder. Figure 1 shows a series of calculations of MAE for $(Fe_{1-x}Co_x)_2B$ for different super-cell sizes; the dependence of the MAE on cell size was shown to be particularly large on the Co-rich side.

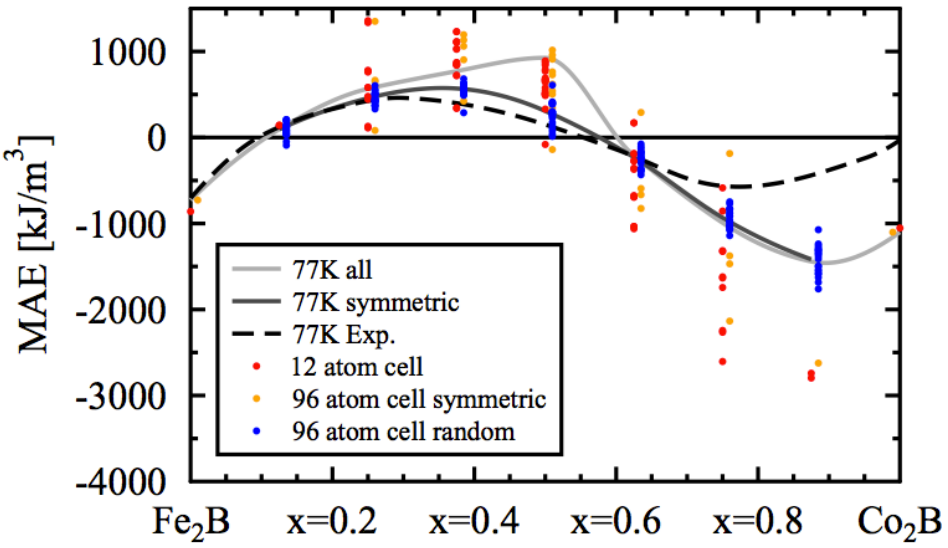

Figure 1: DFT results for the MAE of $(Fe_{1-x}Co_x)_2B$ as a function of Co-concentration, x. See Daene (2015) for details.

Electronic structure of high-entropy alloys: In many applications, the CPA is the method of choice for the prediction of alloy electronic structure and associated magnetic properties. And state-of-the-art Greens function Korringa-Kohn-Rostoker (KKR) DFT codes using the CPA allow for the rapid prediction of properties for complex multi-component systems. Since the search for RE-free materials with favorable properties is likely to involve a

comprehensive examination of such alloys, we participated in a study, jointly with Oak Ridge National Laboratory, to better understand the stability and properties of so-called high-entropy alloys, containing > 4 elements. Figure 2 shows an example of an alloy electron spectral function for the 5-component system MoNbTaVW, as discussed in Troparevsky (2015). Local magnetic moments were also predicted, and comparisons were once again made to super-cell calculations, resulting in increased confidence in high-throughput calculation schemes for certain properties.

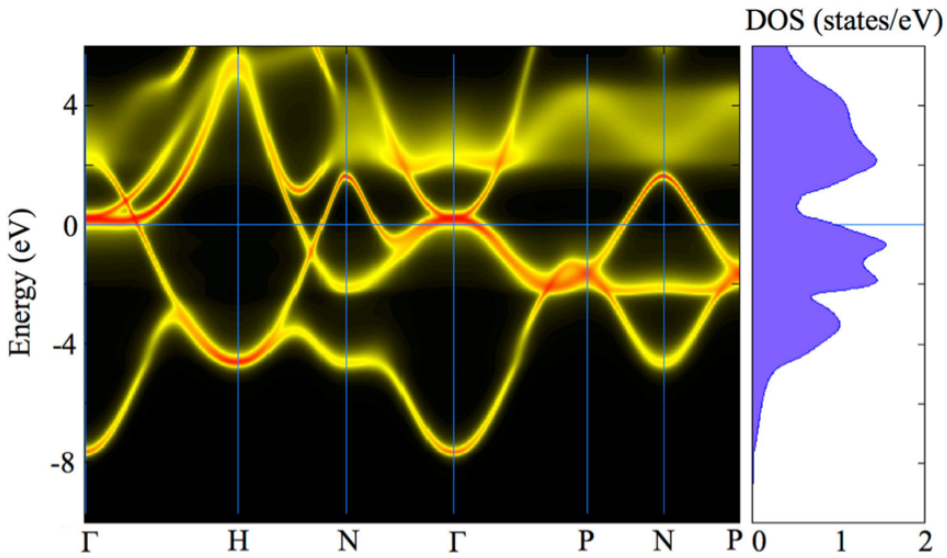

Figure 2: Alloy band structure (electron spectral function) for MoNbTaVW in its bcc phase as computed by the CPA using DFT. See Troparevsky (2015) for details.

Atom-resolved decompositions of the MAE: It is natural to presume that certain ions in a crystal lattice may contribute more to the MAE than others, or that certain ions may favor uniaxial MAE and others planar MAE, etc. As such, we investigated various schemes to decompose the MAE into one-site and multi-site contributions, in an effort to aid the search for materials with favorable properties. The most sensible one-site decomposition proved to be that arising from a λ-integration scheme applied to the SO interaction, in which ground state matrix elements of the SO operator are decomposed into individual ionic contributions (suggested by many researchers in the past). However the usefulness of this decomposition was found to be marginal, due to a fundamental lack of gauge-invariance. Less sensible still was a decomposition of the MAE using projected single-

particle densities of states. This is described in our technical report, Aberg (2015) (see also references therein). A cluster expansion of the MAE for $(Fe_{1-x}Co_x)_2B$ was also attempted, enabling the description of two-ion contributions, but we found this to be of little practical use as well.

T-dependent MAE- Development of a Monte-Carlo importance sampling scheme based on the Heisenberg-Stoner model: The importance of the T-dependence of permanent magnet properties prompted us to study the ferromagnet, CoPt, at elevated temperature. Using DFT, we computed Heisenberg exchange parameters, $J_{Co\text{-}Co}$, $J_{Co\text{-}Pt}$, $J_{Pt\text{-}Pt}$, and then compared the total energies of the associated Heisenberg model to those of DFT. Figure 3 shows the total energies for different spin configurations, DFT vs. Heisenberg (red). The sizable discrepancy results from improper treatment of the Pt spin moments, and incorrect Co and Pt moment sizes for cases with locally misaligned spins (e.g., high-T configurations) in the Heisenberg model. Far better agreement is found with the more detailed Heisenberg-*Stoner* model [Polesya (2010)], which includes the fact that the Pt moment is largely induced by the local magnetic field due to the neighboring Co spins (blue). With this improved agreement, it should be possible to perform Monte Carlo simulations of the T-dependence of various magnetic properties, including MAE, with importance sampling in which the Heisenberg-Stoner model is used to sample the spin configurations, and the DFT is used more sparingly to evaluate SO and other energies not accessible to the model Hamiltonian. This would improve upon the simpler treatment of spin fluctuations adopted in the the Disordered Local Moment (DLM) approximation. Work along these lines continues.

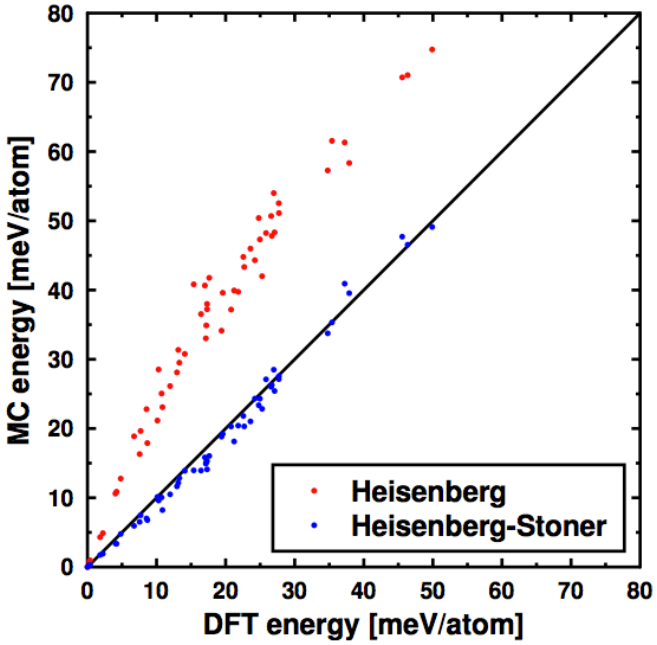

Figure 3: Model Hamiltonian energies vs. DFT energies for super-cells of CoPt with spin configurations sampled from a range of temperatures.

Magnetic structure of uniaxially-compressed Fe: The often subtle interplay between magnetic properties and atomic structure is one of the many features of permanent magnet research that limits predictive capability. Indeed, predicting the energy (and free energy) differences between different magnetic configurations is difficult enough even for ions fixed in position. Decade-old work at LLNL on laser-shocked single-crystal Fe [Hawreliak (2005)] provided us with the perfect opportunity to explore the role of spin fluctuations (i.e., magnons) in the context of time-evolving ionic positions. We constructed generalized Heisenberg models for a range of intermediate crystal structures along the martensitic transformation path from ferromagnetic bcc Fe to antiferromagnetic hcp Fe. Invoking an adiabatic hypothesis in which spin excitations are faster than ionic motion, we then used Monte Carlo with this family of spin fluctuation Hamiltonians to predict the T-dependent transition barriers from bcc → hcp. Figure 4 shows a schematic representation of the transition, in which bcc Fe is strained uniaxially along the [001] direction, and Figure 5 shows our main result: Spin-spiral and anti-ferromagnetic states have much smaller energy barriers than do other magnetic configurations, and Monte Carlo simulation results (not shown) suggest that the experimental findings can be explained by a significant lowering of the barrier due to thermally

excited magnons. Though Fe is not a permanent magnet, this study opens the door to further work on the coupling of lattice distortions and magnons. A publication on this subject is nearing completion [Surh (2015)].

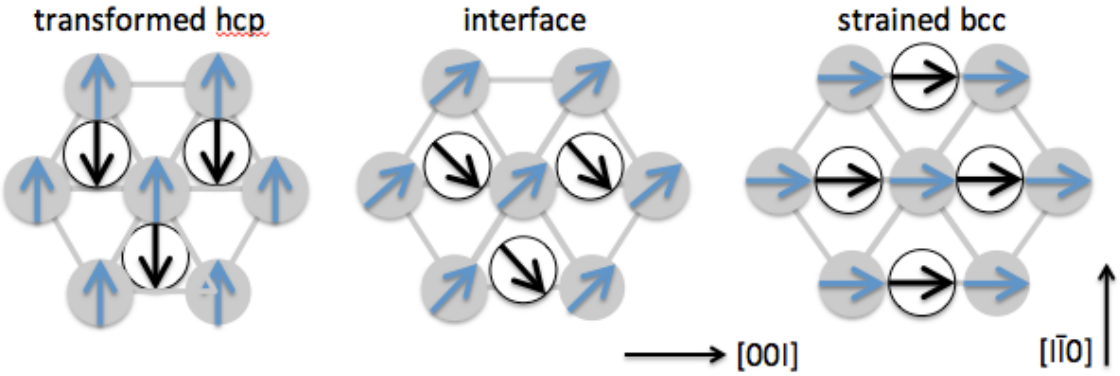

Figure 4: Schematic representation of uniaxially compressed Fe

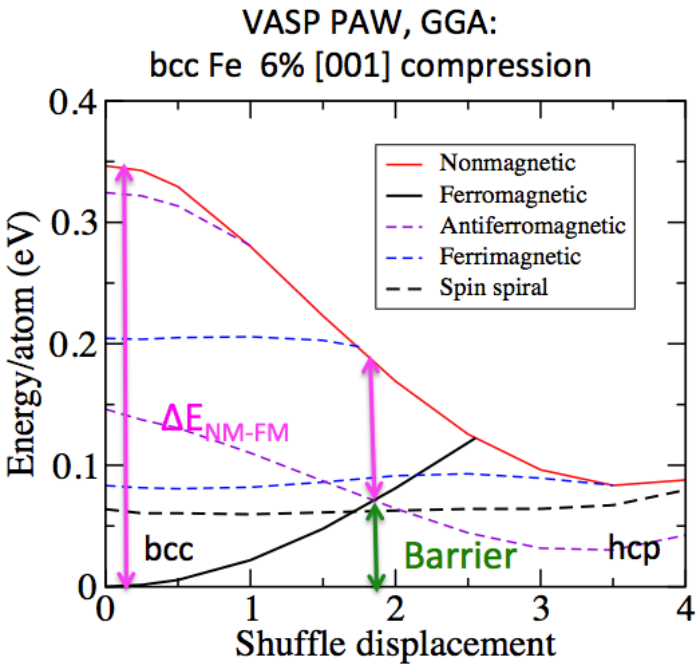

Figure 5: DFT results for the transition barrier between bcc and hcp Fe. See [Surh (2015)] for details.

Investigation of YCo_5 under hydrostatic stress: YCo_5, a non-RE analogue of the RE magnet $SmCo_5$ (cousin to Sm_2Co_{17}), has a sizable MAE which is

greatly underpredicted by standard DFT. It was shown 14 years ago [Steinbeck (2001)] that the addition of Orbital Polarization (OP), a beyond-DFT extension designed to encourage the satisfaction of Hund's 2nd Rule, solves this problem. However, it is often the case that the more fashionable DFT + U method is considered when standard DFT fails. We reinvestigated this problem with both DFT + U (with a value of U chosen to match the ambient-pressure MAE of YCo_5) and DFT + OP. We performed our calculations not only in ambient conditions, but also as a function of moderate hydrostatic stress, since YCo_5 is known to undergo a pressure-driven magneto-structural HS-LS transition [Rosner (2006)]. We found that DFT + OP is indeed the more sensible tool to use, given that the measured HS-LS transition is pushed far too high in pressure if DFT + U with our optimized value of U is used instead [Benedict (2015)].

Impact on Mission

Our work has strengthened LLNL's activities in the Critical Materials Institute, particularly the magnetism thrust area, now entering its 3rd year. In addition, our work on shocked Fe has important implications for a new phase transformation kinetics effort at LLNL (in which two of our members have also become active participants). A postdoc at LLNL, Markus Daene, was converted to full-time staff during the middle of this project, and he currently plays a crucial role in the Critical Materials effort. Our project also hosted (two years in a row) a summer student, Soo-Kyung Kim, soon to obtain her PhD in Materials Science at Georgia Tech partly on the basis of her work with us.

Conclusion

The area of permanent magnet research, particularly the search for RE-free and RE-reduced permanent magnets, is a challenging one. Our incursion into this field has produced promising new tools for us which are being applied both within and outside this immediate area. We expect that our developments in the Monte Carlo simulation of T-dependent magnetic properties will be important for future work within the Critical Materials Institute. And our continued development of ab initio spin dynamics methods, initiated here, will prove important in LLNL's ongoing investigations of the dynamic properties of correlated materials.

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